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A coupled natural immobilisation mechanism for mercury and selenium in deep-sea sediments

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Abstract—In the succession of redox conditions encountered with increasing depth in sediments, the first major redox change is the oxic/post-oxic boundary. The geochemical behaviour of Hg is investigated in three different deep-sea situations where this boundary has been localised within a narrow depth zone for a sustained period (thousands of years) because of changes in sedimentary accumulation conditions. From previous work it is known that a variety of redox-sensitive elements form diagenetic peak concentrations above and below this boundary. This work shows for the first time that Hg also develops sharp peaks immediately into post-oxic conditions in two different situations where sediments containing trace pyrite have been re-oxidised. The Hg peaks are always closely associated with corresponding Se peaks, and the diagenetic concentrations of both elements are persistent over millions of years on subsequent burial into more reducing conditions. There is an apparent offset in the locations of Hg and Se peaks observed in a continuously accumulated case where Se uptake from bottom waters occurs independently of pyrite formation or re-oxidation, which may be a consequence of a widely spread Se peak. It is proposed that formation of the HgSe species tiemannite is involved, by analogy with selenium ore occurrences and the other elements found immobilised along with Se and Hg in the cases studied. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Mercury is a trace element with a natural background level of only ~50 ppb in sediments (Jonasson and Boyle, 1972; GESAMP 1986, 1990), but its high toxicity makes it an environmental contaminant of continuing concern in industrial, mining, and domestic wastes at ppm levels (Lindqvist, 1991; Watras and Huckabee, 1994; Porcella et al. 1995). Elemental Hg(0) and methylated Hg are neurotoxic, while inorganic Hg salts are nephrotoxic (Magos and Webb, 1980). The methylated forms CH₃Hg(II) and (CH₃)₂Hg are of particular concern because they are readily produced from inorganic species in reducing sediments, and then concentrated up the marine food chain (Craig, 1980, 1986a; Bernhard and George, 1986; GESAMP 1986). The high volatility of Hg also prolongs the effects of anthropogenic releases through repeated atmospheric recycling to and from the land and sea (Nriagu, 1989; Mason et al. 1994).

There are three principal marine sedimentary environments where enhanced Hg levels in sediments are found. Most investigations have been made in coastal environments near major industrial or urban discharge points, where recent pollution can increase sediment mercury concentrations by 3–4 orders of magnitude (to 250,000 ppb; GESAMP, 1990) above natural background levels (e.g., Young et al. 1973; Skei and Paus, 1979). Second, naturally enhanced Hg levels are also observed in sediments which are influenced by hydrothermal activity near mid-ocean ridges or other plate boundaries including the compressional type (Jonasson and Boyle, 1972; Bostrom and Fisher, 1969; Toth 1980; Kadko, 1980; Grousset and Donard, 1984). The third Hg-enriched environment is C_{org}-rich (Jonas-

son and Boyle, 1972) or pyritic (Huerta-Diaz and Morse, 1992) reducing sediments.

Mercury has three valency states (I, II, and 0), and the ready interconversion of inorganic and organic forms, including the possibility of disproportionation reactions, means that the environmental behavior of Hg is complex (Jonasson and Boyle, 1972; Craig, 1986b; Rasmussen, 1994). Continuing Hg loss from sediments decades after contaminating Hg inputs had ceased has been demonstrated by following the Hg levels in sediments (Bothner et al. 1980; Gagnon et al. 1997) and biota (Locarnini and Presley, 1996) over time. Although HgS (cinnabar) has a very low solubility, it does not appear to control Hg geochemistry in reducing sediments (Bothner et al. 1980; Gagnon et al. 1997). Huerta-Diaz and Morse (1992) demonstrated that Hg develops a higher content in pyrite than in precursor early diagenetic Fe sulfides, an uptake which probably involves solution transfer of Hg. A consensus of recent investigations is that anoxic sedimentary environments with low sulfide concentrations are conducive to Hg(II) methylation and loss of Hg from sediments (Craig, 1986b; Gagnon et al. 1996).

This paper demonstrates that an efficient natural immobilisation mechanism for Hg exists immediately below the oxic/post-oxic boundary in certain deep-sea sediments. Berner (1981) differentiated the geochemical redox environments in sediments as the oxic, post-oxic, sulfidic, and methanic zones, based on the zonal concentrations of oxygen and sulfide in sediment pore waters. The first major redox change encountered in this scheme is the contrast at the oxic/post-oxic boundary, where post-oxic is defined as the intermediate zone with negligible pore water O₂ or H₂S concentrations between oxic (free O₂ present) and sulfidic (or strongly reducing; free H₂S present) conditions.

Changes in sediment accumulation conditions can cause the

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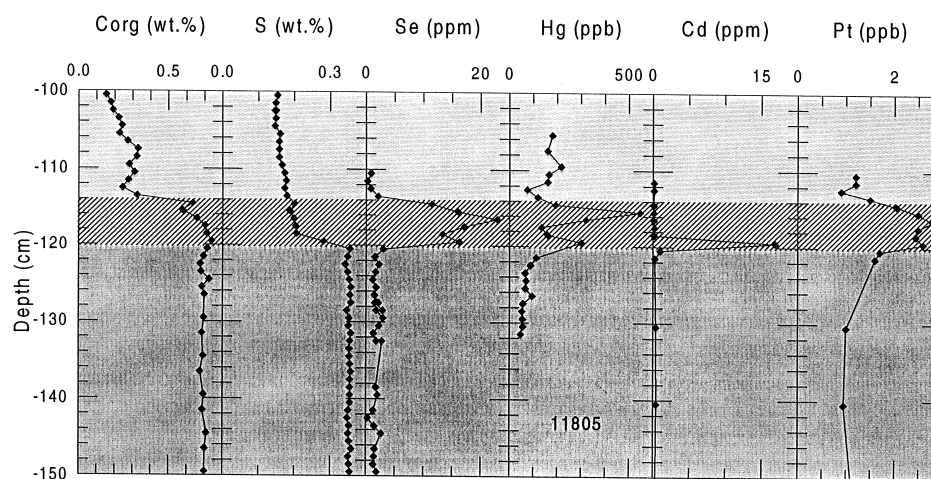


Fig. 1. Concentration versus depth profiles for C_{org} , S, Se, Hg, Cd, and Pt in the distal turbidite in core 11805K (25°39.8'N, 30°57.0'W; 6050 corrected m water depth). Organic C, S, and Se data are from Thomson et al. (1993). Cd data are from Rosenthal et al. (1995) and Pt data are from Colodner et al. (1992). An oxidation front is active at ~120 cm depth below the sediment water interface in this core (Thomson et al. 1993). The lighter and darker tones represent the oxic and post-oxic sections of the same single turbidite unit, while the Se peak is contained within the shaded zone. The shaded zone lies between the step changes seen in the C_{org} and S profiles, is post-oxic, and is intermediate in colour between the overlying oxic and underlying post-oxic parts of this turbidite.

oxic/post-oxic boundary to be localised at a particular depth horizon for a prolonged period. When this occurs, it has been shown that an enrichment sequence of several redox-sensitive elements develops across the boundary, at slightly different depths dependent on elemental geochemistries (Jarvis and Higgs, 1987; Thomson et al. 1993, 1995, 1996). Here the behaviour and response of Hg at this boundary is investigated through study of three different modes of change in sediment accumulation. The first is in discontinuously accumulated sediments (turbidites), and the second and third are in continuously accumulated sediments where either the nature of the accumulated sediments has changed (C_{org} -rich sediments termed sapropels) or the rate of sediment accumulation has changed (transitional glacial/interglacial sediments).

2. METHODS

The sediments available for this study were not collected and processed with analysis for Hg in mind, but instead had been oven-dried at 100°C and ground in agate for major and trace element analysis. This treatment is anticipated to drive off volatile Hg species such as methyl or elemental Hg, so that the results here must be taken as minimum values. The dry powders (200 mg) were prepared for analysis by overnight reflux leach in 5 ml aqua regia (3 volumes c. HCl:1 volume c. HNO_3) at 80°C, filtered through a 0.45 μ m polycarbonate filter, and diluted to 100 ml with H_2O to give a 500:1 volume:mass solution. An aliquot of this digest was analysed directly for Hg by atomic fluorescence spectrometry, using an automated cold vapour generator (PSA Model 10.003). A further fourfold dilution of the digest solution in 40% HCl was analysed for Se by hydride-generation atomic fluorescence spectrometry, using an automated generator (PSA Model 10.001). The accuracy of the method was <2% for both elements when applied to USGS reference materials (marine sediment MAG-1, estuarine sediment BCR-277, and jasperoid rocks GXR-1 and GXR-2). The detection limit was 1 ppb in the sample.

Organic C (C_{org}) data were determined by coulometry, with $CaCO_3$ measured from the CO_2 liberated by 10% phosphoric acid, and C_{org} by subtraction of $CaCO_3-CO_2$ from the CO_2 liberated on total sample

combustion at 900°C. Sulphur was measured by wavelength dispersive x-ray fluorescence (XRF) on powder pellets.

3. RESULTS

The location of the oxic/post-oxic boundary in the cores selected for this study of Hg behaviour has either been proved by pore water studies, or can be inferred because of clear similarities with such studies. In all cases, other compositional data have already been gathered as indicated in the selected cores which demonstrate that a range of other redox-sensitive elements form diagenetic peaks around the oxic/post-oxic boundary. The new Hg data have been collected in three situations.

3.1. Turbidites

The effects of a downwards-migrating progressive oxidation front are particularly evident in organic-rich, distal deep-sea turbidites, because such units are vertically homogenous in composition on emplacement. At the low rates of sediment accumulation in the deep sea, oxidation acts on the upper surface of the turbidite after emplacement for a sustained period, typically tens of thousands of years, and the extent of this post-depositional oxidation by bottom waters is marked by a sharp colour contrast and change in C_{org} content below the top of the originally homogenous unit. Diagenetic enrichment peaks of redox-sensitive metals are found above and below this colour change, dependent on elemental geochemistry (Jarvis and Higgs, 1987; Thomson et al. 1993).

Mercury is now also shown to form a peak in this sequence (Figs. 1 and 2). In the core 11805 turbidite (Fig. 1), the oxidation front has been active for the past 250 ky up to the present (Thomson et al. 1993). By contrast, the core 157-950A-17H-3 turbidite (Fig. 2) was recovered by ocean drilling pro-

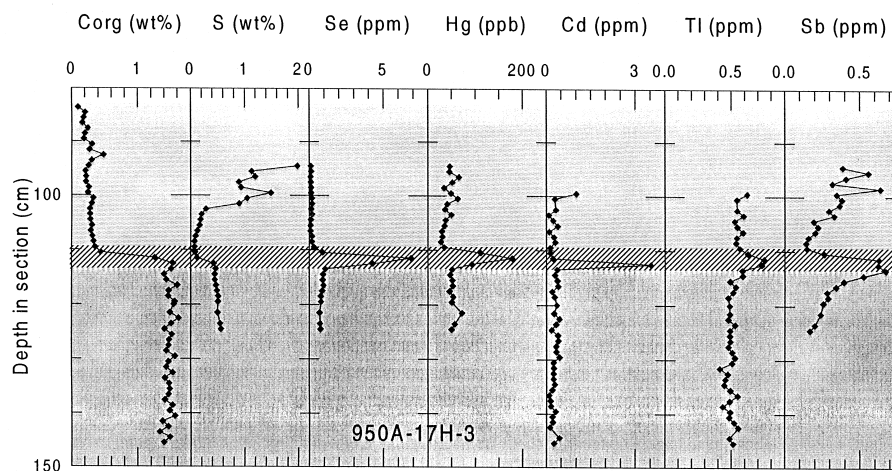


Fig. 2. Concentration versus depth profiles for C_{org} , S, Se, Hg, Cd, Tl, and Sb unit in the turbidite unit in ODP core 157-950A-17H-3 ($31^{\circ}9.01'N$, $25^{\circ}36.00'W$; 5438 corrected m). Depths are cm in core section, but in fact this section is now 153 metres below the sea floor (Thomson et al. 1998). An oxidation front was active in this unit ~ 4 My ago. Data except Hg are from Thomson et al. (1998). The lighter and darker tones represent the sections of the same sapropel unit which were oxic or anoxic during the short period when the oxidation front was active, while the shaded area highlights the Se peak zone.

gram (ODP) drilling from a depth of ~ 150 m below the sea floor. In this case the oxidation front was active for the first few tens of thousands of years after emplacement, but since then the unit has been buried for ~ 4 My with the colour change persisting as a fossil trace of the oxidation front (Thomson et al. 1998). Elements which migrate into oxic conditions at an active front (Mn, I, Fe) are still in place in the core 11805 turbidite, but in the core 950A-17H unit the diagenetic enrichments of these elements have been lost by reduction on deeper burial. Other elements which form peaks in post-oxic conditions (e.g., Se, Cd, V, Sb, and Tl) are present as sharply defined concentration peaks in both units (Thomson et al. 1993, 1998).

3.2. Sapropels

Sapropels are dark, unusually C_{org} -rich (>2 wt%) sedimentary units, formed episodically in the sediments of the Eastern Mediterranean Sea (e.g., Rohling, 1994). They are found intercalated with C_{org} -poor sediments, and it is inferred that sapropels represent short episodes of high surface ocean productivity and/or bottom water anoxia in this restricted basin, which is otherwise oligotrophic, well-oxygenated, and deposits C_{org} -poor sediments. Recent work has revealed that the upper faces of sapropels commonly experience post-depositional oxidation after productivity and bottom water oxygen levels return to the levels at which C_{org} -poor sediments accumulate (Thomson et al. 1995; van Santvoort et al. 1996; Jung et al. 1997). This process thins the original sapropel thickness by oxidation of C_{org} -rich sediment from the top downwards, and is responsible for the sharp visual upper boundary of the unit. Many of the same elements found to develop diagenetic enrichment peaks in deep-sea turbidites form similar peaks around the oxic/post-oxic boundary in sapropels, with the Mn, I, and Fe peaks in oxic conditions and Se, V, Cd, U, and Mo peaks in anoxic conditions (Thomson et al. 1995). Mercury also forms a peak at

this oxidation interface, as shown in the two selected examples of the most recent sapropel, S1 (Fig. 3).

3.3. Glacial/Interglacial Transition Sediments

In the Atlantic Ocean, glacial sediments are generally found to accumulate more rapidly than interglacial sediments (e.g., Bacon, 1984). At glacial/interglacial transitions, as a consequence of the fall in the accumulation fluxes, a slow-moving oxidation front can develop downwards into the uppermost glacial sediments. Thomson et al. (1996) demonstrated that many of the elements which form diagenetic enrichment peaks at oxidation fronts in turbidites or sapropels also form similar peaks in such glacial/interglacial transition sediments. For the last two glacial/interglacial transitions, it was found that well-separated peaks of Mn, Fe, As, and P were observed under oxic conditions in the sediments of the last transition where the oxic-post-oxic boundary was still actively maintained, but not at the previous transition where pore water conditions had become anoxic. In contrast, Se, Cd, V, and U peaks were observed under post-oxic conditions at both of the last two glacial/interglacial transitions (Thomson et al. 1996). Although the Se peak at the active boundary in core CD63#9K is within a factor of 5 of the other Se peaks previously discussed, the $\times 2$ enrichment of Hg is not exactly coincident with the peak Se values but rather the Hg maximum is located 7 cm above the Se maximum (Fig. 4). This offset will be considered further later.

4. DISCUSSION

Well-developed Hg peaks are observed close to the oxic/post-oxic boundary in all the turbidite and sapropel profiles studied. In three cases the oxidation front is currently active (Figs. 1 and 3) but is inactive in one (Fig. 2). This Hg peak formation occurs at a depth close to, but not exactly coincident with, the maxima of similar Se, Cd, Tl, Sb, and Pt diagenetic

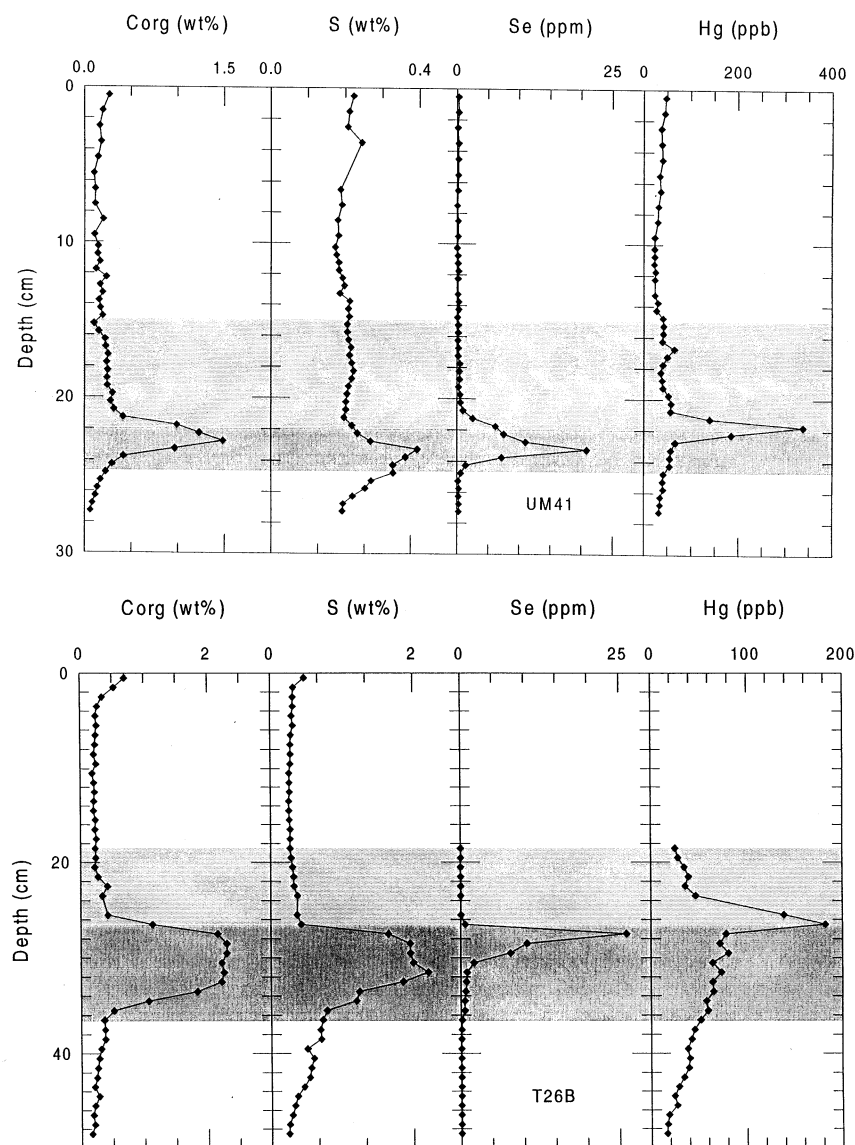


Fig. 3. Concentration versus depth profiles for C_{org} , S, Se and Hg in two cores containing the most recent Eastern Mediterranean sapropel, S1. Core UM41 is at $34^{\circ}57.26'N$, $17^{\circ}51.37'E$; 1390 m (Corselli, 1994), while core T87-26B is at $33^{\circ}38'N$, $28^{\circ}26'E$; 3295 m (Troelstra et al. 1991). In this case the lighter shading represents the amount of S1 oxidised since deposition, while the dark shading represents the remaining unoxidised S1 unit.

peaks (Colodner et al. 1992; Rosenthal et al. 1995; Thomson et al. 1998). Within the resolution of sampling in all four examples, the Hg peak is either coincident with, or on the upper face of, a corresponding Se peak.

No persuasive Hg peak is observed at the active front in the glacial/interglacial profile coincident with the Se peak (CD63#9K; Fig. 4, but see also below). The most obvious difference between the sediments in CD63#9K and the turbidite and sapropel examples is that the sediments in the last two cases contained trace pyrite before re-oxidation to source both the Hg and Se enrichments, whereas the first did not. The situation of a sapropel before oxidation is demonstrated by the elemental profiles of the S1 sapropel in core LC21 (Fig. 5). Unlike the two S1 examples of Fig. 3, this example has suffered very little post-formation oxidation because it was accumulated

at a rapid rate, $\sim 15 \text{ cm ky}^{-1}$ (estimated from unpublished radiocarbon data). In core LC21 it is clear that C_{org} , S, Se, and Hg are all well-correlated to a first approximation. Note, however, that even here there are slight enrichments in the Se and Hg profiles at 141–145 cm at the very top of the sapropel unit which are not present in the C_{org} and S profiles, consistent with a brief episode of oxidation. Mercury is one of the elements preferentially enriched in authigenic pyrite (Huerta-Diaz and Morse, 1992), and Se is also concentrated at greater or lesser levels of enhancement in pyrite (Simon et al. 1997), and this is believed to be the major source of Se in the sapropels and turbidites investigated. The Se peak observed in core CD63#9K, on the other hand, was developed without previous incorporation into sulfide, however, and instead it must have been supplied by downwards diffusion from bottom waters to

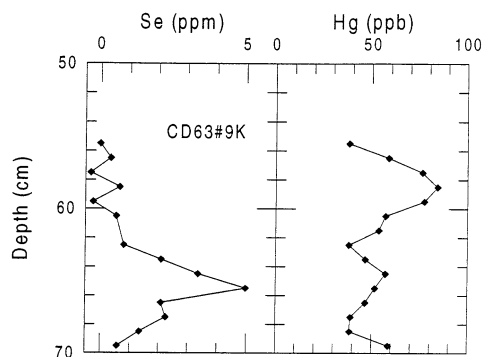


Fig. 4. Concentration versus depth profiles for Se and Hg in core CD63#9K (46°23.8'N, 12°32.8'W; 3849 m). Although this core exhibits a diagenetic Se peak which has been developed just below the active oxic/post-oxic boundary by downwards diffusion from bottom waters (Thomson et al. 1996), the corresponding Hg peak, if real, is offset by 7 cm upwards. See text.

have been immobilised by reduction. A bacterially mediated reduction mechanism for Se to Se(0) has been demonstrated by Oremland et al. (1989) to occur in sediments. In effect it is similar to reduction mechanisms which enrich V and U from bottom waters into anoxic sediments, and indeed U and V enrichments are present deeper in core CD63#9K (Thomson et al. 1996). By inference, such a mechanism might also augment Se peaks on sulfide diagenesis in turbidites and sapropels. In core 11805 (Fig. 1), the amount of Se estimated to be present in the peak ($0.82 \mu\text{mol cm}^{-2}$ Se at an assumed dry bulk density of 0.75 g cm^{-3}) slightly exceeds that estimated to have been released by oxidation from above the peak ($0.77 \mu\text{mol cm}^{-2}$), consistent with a slight additional uptake of Se from bottom waters.

In the work cited above, it has been found that Se forms a peak immediately below that of Fe at stalled oxic/post-oxic

boundaries. Elemental Se(0), FeSe, and FeSe₂ (ferroselite) are the species predicted to control Se solubility in moderately reducing conditions (Masscheleyn et al. 1991). Myneni et al. (1997) have found experimentally that Fe(II, III) "green rust" abiotically reduces Se(VI) to Se(0), but as noted above a similar reduction can be achieved bacterially in sediments (Oremland et al. 1989). The mechanism for Fe peak formation in the deep-sea sediments studied here is that Fe²⁺ diffusing upwards from reducing conditions at depth reacts with O₂ at the base of oxic conditions to form Fe oxyhydroxide. As a consequence, such Fe(III) peaks are not persistent when the sediments are buried and become anoxic (Thomson et al. 1996). The Se peak on the other hand is persistent, as demonstrated by the 4 My old 950A-7H turbidite example (Fig. 4). It is therefore inferred that Se is being immobilised in turbidites and sapropels as soon as post-oxic conditions are encountered (i.e., immediately below, and independent of, the corresponding Fe peak). If independent of Fe, this may involve the formation of Se(0) or selenides.

Two principal factors must be involved in the development of sharp enrichment peaks of Hg, Se, and other redox-sensitive elements in the vicinity of localised oxic/post-oxic boundaries. First, a redox gradient exists across the boundary, imposing thermodynamic controls on elemental speciation, which leads to the development of peaks at slightly different depth levels for different elemental geochemistries. Second, the prolonged (ky) maintenance of this redox gradient at more or less the same locus allows energetically favoured reactions with slow kinetics to proceed towards completion. On this reasoning, the reduced Hg and Se species forming peaks must not only be highly unstable towards O₂ so that they are readily dissolved when overtaken by an advancing oxidation front, but must also be highly insoluble in anoxic (post-oxic) conditions to re-form solid phases immediately below the front. Migration must take place through an oxidised species released to pore water solution, which is reduced and again immobilised in reducing

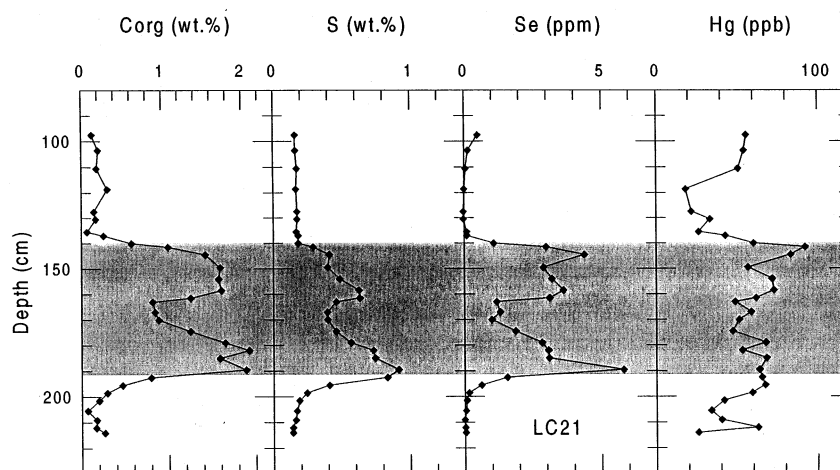


Fig. 5. Concentration versus depth profiles for C_{org}, S, Se, and Hg in eastern Mediterranean core LC21 (35°39.71'N, 26°34.96'E; 1522 corrected m; Rothwell (1995)). Unlike the cores in Fig. 3, the S1 sapropel in this core has been little affected by post-depositional oxic diagenesis because of its rapid accumulation rate ($\sim 15 \text{ cm ky}^{-1}$, from unpublished radiocarbon data). As a result, a good correlation is still retained between all four elements within the C_{org}-rich unit between 140 and 191 cm in core (shaded). Note, however, that even here there are higher Hg and Se values at the very top of the sapropel unit (140–145 cm), consistent with *trace* post-depositional oxidation.

conditions. In the case of the core 950A-17H turbidite (Fig. 2), the well-developed Hg and Se peaks are still in place at the relict boundary of oxidation which can still be identified from the colour change and the C_{org} profile in the turbidite. This demonstrates the long-term stability of such peaks once formed, over 4 My and 150 m of burial, first in post-oxic and subsequently in sulphidic conditions on progressive burial and compaction (Thomson et al. 1998).

At the trace concentration levels of Hg and Se observed, the changes in chemical speciation which are involved in formation of the diagenetic enrichment peaks, and in their continuous dissolution and re-immobilisation when the oxidation front is active, cannot readily be determined directly but must instead be inferred from geochemical behaviour and thermodynamic predictions. Thermodynamic stability predictions for most elements have been assembled by Brookins (1988). Simon and co-workers have recently investigated the stability fields of binary selenide minerals relative to the elements (Simon and Essene, 1996; Simon et al. 1997), but Simon and Essene (1996) point out that the thermodynamic properties and speciation of aqueous Se species remain uncertain. The predicted nonionic forms of Hg at near-neutral pH values (as found in marine sediments) and around redox potential $E_h \sim 0$ V (as found at the oxic/post-oxic boundary) are Hg(0) and HgS (Brookins 1988). The elemental Hg(0) form is both sparingly soluble and volatile, and appears unlikely to be the Hg species that forms the peaks in post-oxic conditions, particularly in view of its persistence as a sharp peak in the ODP turbidite unit over 4 My. Although post-oxic conditions are defined as having negligible O_2 and H_2S levels, it is possible that sufficient trace sulfide may be available to form HgS. This was the explanation advanced by Rosenthal et al. (1995) to explain similar diagenetic Cd peaks in turbidites. The problem for Cd is similar to that for Hg, i.e., to explain a large Cd peak when the thermodynamically predicted insoluble form is CdS. Although HgS is highly insoluble, it does not appear to control the solubility of Hg, even in near-shore anoxic sulphidic sediments, and rather Hg is either incorporated into pyrite (Huerta-Diaz and Morse, 1992; Masscheleyn et al. 1991) or methylated (Gagnon et al. 1996, 1997). In fact, the description of geochemical conditions for Hg methylation by Gagnon et al. (1996) is similar to that inferred here in the formation of the Hg peaks.

An alternative and more likely explanation for the Hg profiles is that there is an interaction between Se and Hg rather than between S and Hg. This is suggested by the fact that, at the most detailed sampling resolution employed (cores 11805, UM41, and T87-26B, Figs. 1 and 3), the Hg peak is always located on the upper face of the Se peak. Selenide minerals, including tiemannite (HgSe), are recognised in certain types of ore deposit (Simon and Essene, 1996; Simon et al. 1997), but such deposits are relatively rare because they require that the ore formation process separates Se from S in order to avoid the substitution of Se into sulfide minerals. Selenium minerals can also form in the weathering zone of S-bearing minerals (Simon et al. 1997), a situation most similar to the cases studied in this work. Separation of Se from S is usually achieved by oxidation, and a large thermodynamic field exists in neutral pH conditions and low oxidation potential where the mobile species are SO_4^{2-} and HSe^- (Simon et al. 1997). In the turbidite and sapropel sediments studied here, it is re-oxidation of pre-existing sul-

fides (e.g., Fig. 5) which has been the principal source of Se and Hg to form the diagenetic peaks (e.g. Figs. 1, 2 and 3), rather than sea water. We speculate that, in the turbidites and sapropels, oxidation has released pyrite S as SO_4^{2-} , which has been lost back to bottom waters by diffusion because conditions are insufficiently reducing in the downwards direction to re-reduce SO_4^{2-} back to sulphides. In contrast, any Se released to solution (whether as SeO_4^{2-} or as less oxidised species $HSeO_3^-$, SeO_3^{2-} , or as HSe^{2-}), must be efficiently reduced again (to Se(0) or selenides) in the downwards direction under anoxic conditions. As noted above, the core CD63#9K Se peak also proves that post-oxic redox conditions can produce an uptake of Se from bottom waters (Oremland et al. 1989), independent of both S uptake by reduction from seawater SO_4^{2-} , and of oxidation of pre-existing sulphides.

In their investigation of selenium ore occurrences, Simon and Essene (1996) and Simon et al. (1997) have shown that a wide range of elements can form binary and more complex selenide minerals if sufficient separation of Se from S is achieved during formation. Dependent on degree of separation and the exact geochemical conditions at the time of formation, these minerals include diverse selenides of low abundance elements such as Ag, Au, Cd, Hg, Sb, and Tl, as well as of more abundant chalcophile elements such as Cu, Ni, and Zn. The former set of elements appear to form selenides at lower Se and S fugacities than the latter set. The mineralogy and the amount of selenide formed from an oxidising fluid is a function of Se, S, and O_2 fugacities and ultimately the solution Se concentration. In the turbidite examples (Figs. 1 and 2), peaks of Cu, Co, Ni, and Zn are formed below the oxidation front (Thomson et al. 1993), but these are mainly located below the Se peak. They cannot be binary selenide-associated because there is insufficient Se to balance the molar amount in the diagenetic peaks of these elements. Also these four elements clearly migrate over short distances on burial after the cessation of the oxidation front, unlike Se, Hg, Cd, and Tl (Thomson et al. 1998).

Formation of selenides could also explain the Cd and Pt peaks previously reported in the core 11805 turbidite by Rosenthal et al. (1995) and Colodner et al. (1992), respectively (Fig. 1). The active oxidation depth in this core is deep in the sediment at ~ 120 cm, and the redox gradient, as inferred from the spectrum of elements immobilised around the oxic/post-oxic boundary, is spread over several cm (Thomson et al. 1993). In this core there is clear evidence that S (as sulfides) in the turbidite is oxidised before C_{org} , and the Se peak is found entirely within with the intervening zone with low S but high C_{org} contents. In the turbidite cores studied, the elemental enrichments occurring with Se are zoned, consistent with some gradation of redox conditions across the Se peak. In all cores (including the sapropel examples), the diagenetic Hg enrichments are located mainly on the upper side of the corresponding Se peak. In cores 11805 and 950A-17H-3 (Figs. 1 and 2), Pt is located over the entire Se peak while the Cd, Tl, and Sb peaks occur at the base of the Se peak. Both Cd peaks are very sharp, but those of Pt, Tl, and Sb are spread over a few cm. Selenium is a more abundant element than Hg, Cd, Pt, Tl, or Sb, and the amount of diagenetic Se in the peaks is much greater than the molar sum of the concentrations of those individual elements inferred here to be immobilised as selenides. Even at the large Cd peak in core 11805 where the

concentration levels of Cd and Se are similar, we estimate that the 1 cm sample with maximum Cd content contains $0.11 \mu\text{mol}/\text{cm}^{-2}$ Cd but $0.14 \mu\text{mol}/\text{cm}^{-2}$ Se (Fig. 1). It is not clear whether the additional Se not balanced by the trace elements identified in these peaks is present as Se(0) or whether it is complexed as selenides of other unidentified elements. It has only been possible to identify the redox-sensitive elements with a probable Se association because (like Se itself) their diagenetic concentration is large compared with their detrital concentration.

The difference in elemental abundance may be the reason for the offset between the smaller peaks observed for Se and Hg in core CD63#9K (Fig. 4). The width of the redoxclines is in the order $\text{CD63\#9K} > \text{turbidites} > \text{sapropels}$, and the magnitude of the elemental enrichment peaks is in the reverse order. It is possible that there is sufficient diagenetic (as opposed to detrital) Se on the upper side of the CD63#9K Se peak to react with the 20–30 ppb of diagenetic Hg, sufficient to form HgSe and hence produce the observed 7 cm peak offset (Fig. 4). Similar considerations apply to the downwards tail in the small Sb peak of in core 950A-17H-3, which appears to persist deeper than the corresponding Se peak (Fig. 2).

Antagonistic biochemical reactions between Se and Hg and between Se and Cd are well known in mammalian toxicology, to the extent that Se has been considered as an effective protection agent against the acute toxicities of both Hg and Cd (Magos and Webb, 1980; Byrne et al. 1995). A 1:1 atomic correlation between the contents of Se and Hg in certain organs (e.g. livers, brains) of marine mammals was first noted by Koeman et al. (1973), and has been verified by subsequent work (Pelletier, 1985; Palmisano et al. 1995; Nigro and Leonzio, 1996). This correlation is not inherited from the food source, because Hg is predominantly present in fish as $\text{CH}_3\text{Hg(II)}$. Formation of HgSe in mammals is therefore generally inferred to be the end result of a biochemical detoxification pathway involving Hg demethylation (Magos and Webb, 1980; Byrne et al. 1995). Martoja and Berry (1980) have unambiguously identified particles of the mineral tiemannite (HgSe) in cetacean livers.

An attempt was made in this work to identify tiemannite in selected sapropel samples with the highest Hg and Se contents. Freeze-dried, resin-impregnated, and polished thin sections were examined by scanning electron microscopy using back-scattered electron and energy dispersive spectroscopy-XRF analysis. The backscatter electron technique is sensitive to variations in atomic number (Z), and it was hoped that micrometer-sized grains of tiemannite (if present) would stand out against the lower Z of background aluminosilicates. No such grains were identified, but it is possible that oxidative destruction of any such grains during section preparation might have occurred.

5. CONCLUSIONS

Diagenetic redistribution peaks of Hg are reported from compositionally well-characterised deep-sea sediment cores. These are found at active and fossil occurrences of the oxic/post-oxic boundary in turbidites and sapropels where oxidation of pre-existing sulfides is involved, and less certainly in a continuously accumulated section with an active oxic/post-oxic

boundary where a Se peak is forming without accompanying sulfide formation. The Hg peaks are always coincident with the associated Se peaks, and by analogy with Se ore geochemistry it is proposed that formation of HgSe (tiemannite) occurs following Se separation from S after sulfide oxidation. This selenide formation mechanism following oxidation of precursor sulfides may apply to other trace elements such as Cd and Pt which also appear to form peaks in close association with Se.

Coupled Se and Hg peaks at the tops of sulfide-rich sedimentary units are therefore likely to be permissible indicators that post-depositional oxidation of the units has occurred. Sulfide wastes are often enriched in Hg, and their oxidation in the environment can give rise to environmental toxicity problems through release of associated elements (e.g., Morse, 1991; Cooper and Morse, 1998). The findings here suggest that Hg loss from oxidation of sulfides may be retarded so long as sufficient Se is present, and so long as competitive sulfate reduction does not remain active in the waste (Di Toro et al. 1990).

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